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THE COMBUSTION OF THREE-COMPONENT CONDENSED MIXTURES

N. N. Bakhman and Yu. A. Kondrashkov

Suppose we take a mixture of two gasifying components* (e.g., KClO_4 + bitumen) and introduce into it a certain amount of non- /216

volatile particles (e.g., tungsten). Let the rate of combustion of the basic mixture be u_0 cm/sec, and the rate of combustion of the

mixture with the added particles u cm/sec. The ratio u/u_0 shows the variation in the rate of combustion on introducing a given impurity.

Let us now consider how the quantity z will vary with variation in the dimension d of the non-volatile particles.

1. For sufficiently large d we should get $z \rightarrow 1$, i.e., the addition of sufficiently large particles should not affect the linear rate of combustion of the basic system. In fact, sufficiently large particles can ignite and burn only at points remote from the combustion front of the gasification products of KClO_4 and bitumen** and therefore cannot transfer to fresh material any sub-

* Components (originally solid) which first gasify and only then mix and burn. On the basis of the work of P. F. Pokhil [1], it may be assumed that the gasification of oxidizers and, less probably, of organic fuels is accompanied by their partial dispersion in the form of very fine particles. This extends the zone of gasification and complicates the whole process.

**We shall consider the case where the size of the KClO_4 particles (d_{ox}) is sufficiently small, so that the combustion front of the gasification products of KClO_4 and bitumen is plane and combustion proceeds under kinetic conditions [2, 3].

stantial part of their heat of combustion. On the other hand, the heat losses due to preheating and phase transformations of the large particles in the zone between the fresh material and the combustion front are also small. In this case the rate of combustion is determined by the rate of volume heat release due only to combustion

of the gasification products of KClO_4 and bitumen (Φ_1 , cal/cm³·sec)

at a temperature somewhat less than the temperature at the combustion front of the basic mixture (without added particles), the composition of the gas being the same.

2. Let us now turn to the case of sufficiently small added particles. There is a certain particle size d^* such that when $d \leq d^*$ the particles will ignite and burn completely in the zone between the fresh material and the combustion front of the gasification products. The order of d^* can be estimated from the condition

$$t_c \leq t_d \quad (1)$$

where t_c = combustion time of particle, and t_d = dwell time of particle in zone with temperature lying between T_i (ignition point) and T_f (temperature at front).

We shall take

$$t_c \approx \frac{\rho_p d^2}{8\rho_g D_g \ln(1+B)},$$

where ρ_p , ρ_g = density of particles and gas (gasification products),
 D_g = diffusion coefficient, B = transport parameter [4]. We shall
 further take

$$t_d \approx \frac{a_g}{vw} \ln \frac{T_f - T^*}{T_i - T^*},$$

where (see [5])

$$T^* = T_s - \frac{c_m (T_s - T_o) + q_o}{c_g};$$

where a_g , v = thermal diffusivity and velocity of gas, w = velocity
 of particles, c_m = mean heat capacity of the condensed phase
 (k-phase), T_s = temperature at surface of k-phase, q_o = heat of
 gasification of the binary mixture $KClO_4$ + bitumen. In practice,
 when $d \leq d^*$ we can take $w \approx v$. Then from (1) we get:

$$d^* \approx \frac{a_g}{v} \sqrt{8 \frac{\rho_g}{\rho_p} \ln(1+B) \ln \frac{T_f - T^*}{T_i - T^*}}, \quad (2)$$

i.e., d^* is proportional to the width of the zone between the front and the surface of the k-phase ($\sim a_g/v$), but less than the latter

(since $\rho_g/\rho_p \ll 1$). When $T_i = T_f$, d^* vanishes; the maximum value of d^* is attained when $T_i = T_s$. Equation (2), however, does not permit

a numerical evaluation owing to the indeterminacy of the method of computing the parameter B and the absence of reliable data on the ignition point. It is clear only that d^* is very small and, for example, at 1 abs. atm. scarcely exceeds a matter of tenths of a micron for the system in question.

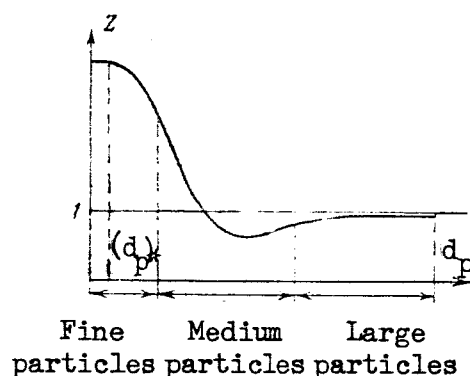
/217

3. When $d < d^*$, the interaction of the components falls into two spatially separate stages: first the particles react with the gasification products of $KClO_4$, then there follows a reaction

between the gasification products of bitumen and the remaining part of the gasification products of $KClO_4$. In multi-stage combustion

there is ordinarily a single leading stage, which is responsible for the experimentally observed rate of combustion, the other subordinate stages being obliged to adjust themselves to this rate as a result of heat transfer from the leading stage. The subordinate stages themselves (without heat transfer from the leading stage) would either be quite incapable of sustaining the propagation of the flame or give a lower rate of combustion. Naturally, the subordinate stages can themselves influence the rate of combustion, but their influence is only indirect: if the velocity of a subordinate stage of the reaction is varied, the rate of combustion will vary only to the extent that the velocity of the leading stage is affected. If (for example, by adding a very small amount of particles acting only on a subordinate stage) we vary the velocity of a subordinate stage of the reaction, without affecting either the temperature or

the composition of the reagents in the leading zone, there will be absolutely no change in the rate of combustion.



From the above it follows that on adding a given, not too great percentage of non-volatile particles, such that the combustion of the particles is not the leading stage, the rate of combustion should remain quite unaffected by a further (below d^*) reduction in the size of the particles* or by a reduction in T_i (so long as $T_i > T_s$). For example, following a sudden reduction in T_i the particles

begin to ignite and burn closer to the surface of the k-phase, the flow of heat to the fresh material is intensified, and there is a corresponding increase in the rate of gasification. The combustion front, however, cannot deal with the increased flow of gasification

Strictly speaking, this will occur for a particle size less than the d^ from (2), since it is necessary to take into account not only the combustion time of the particle but also the time for the temperature to equalize over the flow cross section.

products (since neither the temperature at the front nor the composition of the gas is affected) and begins to move away from the surface of the k-phase until the rate of gasification returns to its original value*. Of course, the temperature profile will then be different from the original one. In particular, there will be an increase in the heat fraction reaching the surface of the k-phase from the burning particles, and a decrease in the heat fraction from the combustion front of the gasification products.

When $d < d^*$ (and the percentage of particles added is not too great), the rate of combustion will depend on the rate of volume heat release due only to the combustion of the gasification products, but now at a higher temperature** than for the starting (particleless) mixture and with a gas composition poorer in oxidizer.

4. Finally, given a "medium" particle size, when the combustion zone of the gasification products and the combustion zone of the particles are not spatially separated, the rate of combustion will depend both on $\dot{\Phi}_1$ and on $\dot{\Phi}_2$, where $\dot{\Phi}_2$ (cal/cm³·sec) is

the rate of volume heat release due to combustion of the particles.

Thus, we can expect the curve $z(d)$ to have the form shown in the figure: a plateau when $d < d^*$, an asymptote $z \rightarrow 1$ for large d , and a minimum close to the boundary between medium and large particles**.

* It should be borne in mind that if a sufficiently strong influence is exerted on a subordinate stage it may become the leading stage, and vice versa.

** On condition that the heat of combustion of the particles is sufficiently large.

***Note that the position and value of this minimum also depends on whether the heat conductivity of the particles is sufficiently large or sufficiently small. In the case of metal particles, i.e., particles with high thermal conductivity, the temperature at the surface and at the center of the particle is practically the same (in the range of particle sizes with which we are concerned). The initial heating of a particle is limited by the rate of heat transfer from the gas to the particle. Conversely, in the case of particles with very low thermal conductivities (e.g. particles of charcoal) the temperature at the surface of the particles may be considerably higher than at their center (if the particle is not too small). The initial heating of a particle is limited by its thermal conductivity. In these circumstances, of course, the cooling of the gas by the particles is slower than in the first case.

5. So far the above reasoning has been experimentally verified for the case of large particles. The method employed was similar to that described in [6]. In accordance with the theory, adding large particles of W or Al reduced the rate of combustion of mixtures of KClO_4 + bitumen by not more than 5-15%. For example,

for a mixture of KClO_4 ($d_{\text{ox}} \approx 10 \mu$) + bitumen ($a_o = 0.75$)* + 13.1%

/218

Al ($d = 190 \mu$) the following results were obtained:

p, gauge atm.	0	5	10	50	100
z	0.99	0.96	0.94	0.92	0.96

The experimental verification of the presence of a plateau corresponding to $d < d^*$ is very difficult, since it is necessary to have several very fine (for orientational purposes -- of the order of 0.1-0.01 μ) fractions of the given particles.

6. Apart from the effect of the addition of large particles on z, we were also able to test by experiment another proposition following from our theory, namely that for "medium" particles the value of z (for $d = \text{const}$) should fall with increase in p. In fact, after ignition the particles burn under approximately diffusion conditions [7]. The rate of heat release per unit volume due to particle combustion is then:

$$*a_o = \frac{m_{\text{KClO}_4}/m_{\text{bit}}}{(m_{\text{KClO}_4}/m_{\text{bit}})_{\text{stoich}}}, \text{ where } m_{\text{KClO}_4}, m_{\text{bit}} \text{ are the weight fractions of } \text{KClO}_4 \text{ and bitumen in the mixture.}$$

$$\Phi_2 = \rho_p u_p \pi d^2 N' Q, \quad (3)$$

where u_p = linear rate of combustion of particle, N' = number of particles per unit volume, Q = heat of reaction of particle with oxidizer. Using expression (3.46) in [4] for $\rho_p u_p$ and substituting

$$N' = N \frac{u}{w} = \frac{m_p \rho_m}{\rho_p} \frac{6}{\pi d^3} \frac{u}{w},$$

where N = number of particles per unit volume of k-phase, m_p = weight fraction of particles in k-phase, ρ_m = density of k-phase, we get:

$$\Phi_2 \sim Q \frac{\rho_g^D g}{d^2} \frac{m_p \rho_m}{\rho_p} \frac{u}{w}. \quad (4)$$

In (4) the only factor dependent on the pressure is $u/w \sim p^{n_2}$, where $0 < n_2 < 1$ ($n_2 = 0$ corresponds to the case of large

TABLE 1

Variation in the Rate of Combustion on Adding
 Particles to a Stoichiometric Mixture of
 KClO_4 ($d_{\text{ox}} \approx 10 \mu$) + Bitumen.

Particles, %	d, μ	z				
		0	5	10	50	100 gauge atm.
Al (powder), 13.1	~ 12	1.44	1.30	1.20	1.06	1.04
Zr, 13.1	~ 12	1.88	1.61	1.43	1.13	1.02
Ti, 13.1	~ 16	1.14	1.11	1.07	0.95	0.89
W, 13.1	~ 2.5	1.12	1.10	1.09	1.07	1.01
W, 31.1	~ 2.5	1.38	1.25	1.12	1.04	0.94

particles, and $n_2 = 1$ to the case of sufficiently fine particles). Meanwhile, the rate of heat release due to the reaction of the gasification products Φ_1 is proportional to p^{n_1} , where $n_1 = 1$ for a monomolecular reaction, $n_1 = 2$ for a bimolecular reaction, and so on. Thus, as a rule, Φ_1 increases with increase in p more rapidly than Φ_2 , so that the part played by Φ_2 diminishes with increase in p , which leads to a reduction in z . It should also be borne in mind

TABLE 2

Rate of Combustion of Three-Component Mixtures
 $\{(100 - a)\% [\text{KClO}_4 + \text{Bitumen } (a_0 = 1)] + a\%$

Particles} and the Corresponding
 Binary Mixtures.

Particles, %	Rate of Combustion, mm/sec	Pressure (gauge atm.)				
		0	5	10	50	100
W, 13.1	u	1.12	4.7	7.3	20.8	33.5
	u_0	1.0	4.3	6.7	19.4	33.0
	u'	when $p \leq 100$ gauge atm. will not burn				
W, 31.1	u	1.38	5.37	7.5	20.2	31.1
	u_0	1.0	4.3	6.7	19.4	33.0
	u'	-	3.5*	5.4*	9.2*	12.5*
Al, 13.1	u	1.44	5.6	8.0	23.1	38
	u_0	1.0	4.3	6.7	21.7	36.4
	u'	when $p \leq 50$ gauge atm. will not burn				
Zr, 13.1	u	1.88	6.9	9.6	22	33.6
	u_0	1.0	4.3	6.7	19.4	33
	u'	when $p \leq 100$ gauge atm. will not burn				
Ti, 13.1	u	1.14	4.8	7.2	18.4	29.3
	u_0	1.0	4.3	6.7	19.4	33
	u'	when $p \leq 50$ gauge atm. will not burn				

*S. A. Tsyganov's data for 40% W + 60% KClO_4 . The rate of combustion of 34.2% W + 65.8% KClO_4 (corresponding to the ternary mixture in question) is even lower.

that as p increases a particle of a given size becomes larger and larger in relation to the combustion zone of the gasification products.

The figures in Table 1 show that for "medium" particles experiment actually does give a monotonic decrease in z with increase in p .

7. When a not too great percentage of "medium" particles is added, Φ_2 should be small compared with Φ_1 (taking into

account the change in the temperature and gas composition due to particle combustion). It may be assumed that for the mixtures in Table 1 this condition is fulfilled. In fact, it proved that the binary metal-oxidizer mixtures obtained if bitumen is removed (or more accurately not introduced) from the ternary mixture either, as is generally the case, do not burn or have a rate of combustion u' substantially lower than u and u_0 (Table 2). In other words, the rate of combustion u of the mixtures in Tables 1 and 2 is determined by the rate of reaction of the gasification products of $KClO_4$ and bitumen.

CONCLUSIONS

13974

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1. For systems burning in the gas phase, adding large metal particles has no marked effect on the rate of combustion (reduces it slightly). This is because the particles burn too far from the main zone of combustion, while there is only a slight reduction in the temperature of the combustion zone due to preheating and phase transformations of the particles, provided the latter are sufficiently large.

2. As the size of the metal particles decreases, the heat losses due to the initial heating of the particles increases. At the same time there is an increase in the flow of heat from the zone of particle combustion to the main combustion zone. Accordingly, as the particles are reduced in size, the rate of combustion will pass through a minimum and then increase (if the heat of combustion of the metal is sufficiently large).

/219

3. If the percentage of metal added is not too large, so that the stage of particle combustion is not the leading stage, there exists a minimum size of the metal particles, below which the rate of combustion will stop increasing with further pulverizing of the metal. This minimum size is determined by the condition that the metal particles are able to burn up completely before reaching the main combustion zone.

4. For particles of "medium" size the effect diminishes as the pressure increases, since the rate of the gaseous reactions generally increases with increase in pressure more rapidly than the rate of combustion of the metal particles.

5. This theory has been partially tested by means of experiments with a mixture of $KClO_4$, bitumen, and particles of W, Al, Ti, and Zr.

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